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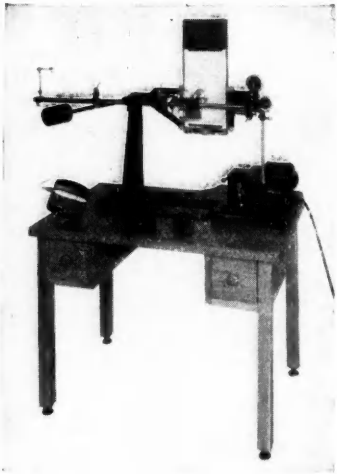

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Microscopic Structure of the Wool Fiber

BY CHARLES W. HOCK, ROBERT C. RAMSAY, and MILTON HARRIS*

A Textile Foundation Publication

Abstract

An investigation was undertaken to obtain information concerning the fine details of structure of wool fibers and especially of their constituent scale and cortical cells. Treatment of chemically modified wool with the enzyme, pepsin, was found to be an excellent method for releasing individual cells for such studies.

It is shown by microdissection that the striated appearance of the cortical cells is due to the presence of many fibrils which can be separated with microneedles. Near the center of each cell is a nucleus which has a granular structure. Between crossed nicols, the fibrillar part of the cortical cells appears birefringent, whereas the nucleus does not.

The scales show little internal organization such as exhibited by the cortical cells. When examined with crossed nicols they appear nonbirefringent. Unlike the cells of the cortex, the scales are not easily separated by treatment with enzymes, but remain attached to each other in a manner comparable to the arrangement of shingles on a roof.

A comparison of root and shaft of the fiber reveals numerous differences in reaction to microchemical color tests, as well as differences in cellular structure. The root, for example, gives a positive test for sulfhydryl groups whereas the shaft gives a negative test. Similarly, the shaft appears birefringent whereas the root does not. These and other observations clearly indicate that as the cells of the root emerge into the shaft a number of physical and chemical changes take place simultaneously.

When wool is placed in chlorine water bubbles arise on the surface of the fibers (Allwörden reaction). Evidence is presented in support of the viewpoint that these bubbles arise solely from the scales and that their formation is associated with the reaction of the chlorine with disulfide groups of the cystine in the scales.

* Research Associates at the National Bureau of Standards, representing the Textile Foundation.

I. Introduction

WOOL fibers are specialized appendages of the epidermis of the sheep, and show many similarities to other skin tissues, such as nails, horns, and feathers. A growing fiber consists of a root and shaft, the former being the living region situated beneath the surface of the skin, whereas the latter is the nonliving portion that extends above the skin surface. Increase in length of the fiber is brought about by the proliferation of new cells in the root and the subsequent emergence of these cells into the shaft. The shaft is composed of dead cellular units which usually are arranged in three layers, an outer layer of scales, a middle region called the cortex, and a central core or medulla. The relative thickness of each of these layers varies considerably in different fibers. Kemp, for example, has a large medulla, whereas in the best grades of wool the medulla is either absent or very small.

Much of this knowledge of the structure of the fiber was contributed by the early researches of Nathusius[1]* and McMurtrie.[2] These investigators obtained considerable information concerning the shape, length, and fineness of wool, and in addition described the various types of cells which comprise the fiber. A number of the structural details were also noted later by Kronacher and Lodeman,[3] von Bergen,[4] Reumuth,[5] and Müller[6] as well as others. In the present investigation these earlier observations have been extended in order to obtain additional information on the fine details of structure of the fibers and especially of their constituent cells.

II. Materials

Two samples of wool were used in the investigation. One consisted of domestic wool, for the most part nonmedullated, which was purified by successive extractions with ethyl alcohol and with ether for 16 hours each, followed by washing with water at 40° C. A second sample was obtained from the Bureau of Animal Industry, U. S. Department of Agriculture.† It consisted of wool carefully pulled from the back of a Hampshire sheep so as to have the roots attached to the shaft, and also of small pieces of skin which were cut directly from the sheep and placed in fixing fluids.

III. Experimental Procedure and Results

1. Separation of cortical and scale cells

When wool fibers are mounted in water and examined with a microscope, much can be learned about the size, shape, and appearance of the surface of the fibers, but very little is learned of the detailed structure of their constituent cells. In order to study the minute structure of the various types of cells, the fibers must be treated in a way that makes a more detailed microscopic examination possible. For this purpose thin cross and longitudinal sections can be employed to good advantage, but the liberation of single cells from the fibers is even more satisfactory.

The liberation of cells from fibers by various chemical reagents, enzymes, and bacteria has been frequently reported in the literature. The treat-

* Figures indicate the literature references at the end of this paper.

† Acknowledgment is made to Dr. J. I. Hardy for supplying this material.

ments with chemical reagents usually involve the use of strong acids or alkalies and are sufficiently drastic to produce more or less profound changes in structure. Treatment of the fibers with enzymes is in many respects more satisfactory and has been used considerably in the present investigation.

Although untreated wool is highly resistant to the action of enzymes, it has been shown in work now in progress in this laboratory [7] that fibers in which disulfide cross-linkages have been ruptured by reduction with thioglycolic acid and then methylated to prevent re-formation of the linkages are rapidly attacked by treatment with an enzyme such as pepsin. Accordingly, it was decided to follow, microscopically, the changes which reduced and methylated wool undergoes in pepsin, in an effort to obtain information concerning the structure and behavior of the cells. For comparison, untreated fibers were similarly examined.* Samples of each were placed in vials containing a solution of the enzyme. At the same time, single fibers were placed in a drop of enzyme on a microscope slide and protected with a cover glass, which was sealed to the slide with vaseline. The latter method made possible the continuous observation of a single fiber over a relatively long period. The specimens were examined and fresh enzyme was added every 2 or 3 days. The experiments were run at two temperatures, one at room temperature (22–25° C) and another at 35° C. The material kept at the higher temperature was the first to show evidence of attack by the enzyme, but otherwise the two series ultimately presented essentially the same microscopic appearance.

In agreement with the other work,[7] it was found that untreated wool was not readily attacked by pepsin. Even after long exposure to the enzyme these fibers showed little evidence of damage except for frayed ends, and sometimes the liberation of a few cortical cells. The reduced and methylated wool was attacked more rapidly. Cells obtained from this wool had the same initial appearance as cells obtained in a similar manner from untreated wool. However, as will be shown later, cells from untreated wool were resistant to further action of the enzyme whereas cells from reduced and methylated samples were eventually digested. With reduced and methylated wool, even at room temperature, changes in the fiber were detectable in less than 24 hours. The free ends of the fiber were usually frayed, and some intermediate parts appeared to be darkened and crushed. After several days pronounced changes had taken place. The fibers had lost their lustre and exhibited a pronounced striated appearance due to the increased prominence of the cortical cells. After continued treatment with enzymes, large numbers of cortical cells were liberated from the fibers (Fig. 1, A, B and C). The cortical cells were removed not only from the ends of the fiber but from intermediate parts as well, leaving in extreme cases practically intact tubes of scale cells (Fig. 1, C). In regions where only part of the cortex was removed from a given area, it was found that the first cells to be liberated lay next to the scales. Additional cortical cells were released upon applying pressure to the cover glass.

The enzyme apparently had easier access to the cut ends of the fiber and thus brought about greater deterioration in those regions. This behavior has also been noted by other investigators. Photomicrographs by

* A solution of pepsin was prepared by dissolving 1 mg. of the crystalline enzyme in 1 ml. of phosphate buffer at pH 1.2. A few drops of merthiolate were added to the solution as a preservative.

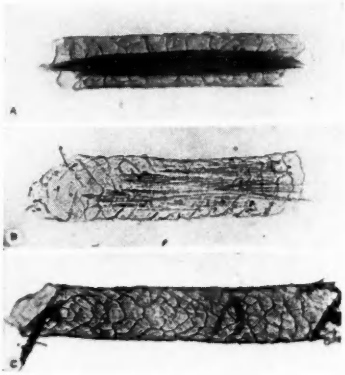

Fig. 1.

Fig. 2.

Fig. 4.

Fig. 4.—Cross section of an untreated wool fiber after several weeks in a solution of pepsin followed by swelling with 9 percent sodium carbonate. The photomicrograph shows the outline of the individual cortical cells and their nuclei. Magnification × 1500.

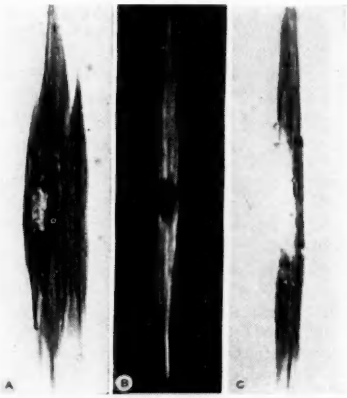

Fig. 3.

Fig. 1.—Reduced and methylated wool fibers treated with solutions of pepsin. A, B, and C show three stages in the removal of cortical cells from the fibers. A and B unstained; C stained with Orange II. Magnification × 350.

Fig. 2.—Cross sections of wool fibers treated with solutions of pepsin. A. Sections of untreated fibers in pepsin for 1 month. B. Sections of reduced and methylated fibers in pepsin for 10 days. C. Section of reduced and methylated fibers in pepsin for 1 month, showing only the thin ring of scales which remains. Magnification × 450.

Fig. 3.—Single cortical cells from reduced and methylated fibers photographed under various conditions. A. Cell, stained with Orange II, showing the nucleus and the fibrillar appearance of the rest of the cell. B. Cell, between crossed nicols, showing the non-birefringent nucleus in the birefringent cell. C. Single cell nearly eaten in two by the prolonged action of pepsin. Magnification × 1400.

von Bergen [4] indicate that after certain chemical treatments the ends show the most damage. From the work of Royer and Millson [8] on dyed wool it is evident, also, that the ends of the fibers take up dye more rapidly than do intermediate parts. Similar results, indicative of the greater liability to attack at the ends, were obtained in the present investigation. Furthermore, when the ends of untreated and of reduced and methylated fibers were sealed with glue before placing the fibers in pepsin, it was found that the breakdown of the fibers was retarded. After a few weeks in the enzyme, however, this difference between fibers with sealed and with unsealed ends was lost, both samples then showing similar degrees of disintegration.

In order to study further the action of pepsin on untreated and on reduced and methylated wool, cross sections, cut 10 to 15 microns thick with the Hardy device,[9] were placed either in vials containing the enzymes or in drops of the latter on microscope slides. Even after a month there were only slight changes in the untreated sections (Fig. 2, A). With sections of reduced and methylated wool the cortex was eaten out, leaving in extreme cases only a thin ring of scales (Fig. 2, C). The degree of breakdown of the wool was related to the length of exposure to the enzyme (compare Fig. 2, B with Fig. 2, C). Furthermore, the rate of digestion appeared to be associated with the extent of reduction of the wool, as reduced and methylated fibers with 90 percent of the disulfide cross-linkages broken were much more rapidly attacked by the enzyme than those in which only 50 percent of the linkages had been disrupted. When free cortical cells, released from partially reduced and methylated fibers upon treatment with pepsin, were placed in fresh enzyme for a period of 1 month, some of the cells appeared to be digested whereas others from the same sample remained practically intact. These differences appear to be associated with the extent of reduction of the wool and suggest that the undigested cells may be ones in which most of the cross-links are intact.

The results of these experiments indicate that the scale cells are resistant to the action of pepsin and that the ease with which single cortical cells are liberated depends on the previous chemical treatments which the fibers received. Although cortical cells may be rapidly separated from each other by the action of pepsin, individual cells show further signs of disintegration only after continued treatment with the enzyme.

2. Structure of the cortical cells

Single cortical cells are spindle-shaped. They vary in size depending on the sample of wool. Walther [10] found that their average size varied from 80 to 110 microns in length, 2 to 5 microns in width, and 1.2 to 1.6 microns in thickness. Cortical cells liberated from fibers by the action of chemical agents frequently show evidence of fimbriated ends. In most cases, also, the cells are prominently striated.

On careful examination of single cells liberated from the cortex by the action of pepsin, a structure located near the center of the cell and resembling a nucleus was frequently observed (Fig. 3, A). This central region did not, however, stain with common nuclear dyes such as hematoxylin and methylene blue. Fig. 3, A shows also that the nucleus is granular, whereas the rest of the cell is fibrillar in appearance.

Nuclei are not easily observed in untreated cross sections, but are clearly visible after the latter have been properly stained or swollen.[5] For

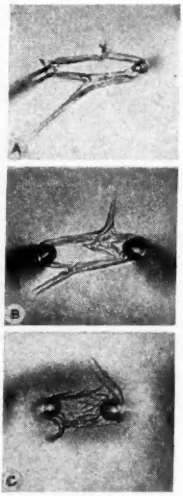

Fig. 5.

Fig. 6.

Fig. 9.

Fig. 9. — Single fiber (pulled from the back of a sheep) treated with sodium nitroprusside. The dark color of the root indicates the presence of sulfhydryl groups. Part of the cuticle of the follicle remains attached to the fiber. Magnification × 120.

Fig. 8.

Fig. 7.

Fig. 5.—Cortical cells being dissected with microneedles to show their fibrillar structure. Magnification × 500.

Fig. 6.—Group of scales released by the action of pepsin on reduced and methylated fibers. Stained with Orange II. Magnification × 1420.

Fig. 7.—Single fiber (recently pulled from the back of a sheep) stained according to Feulgen's technique, showing the dark colored root indicative of a positive test for nucleic acid. Fibers mounted in water. Magnification × 120.

Fig. 8.—Root of a wool fiber showing individual nuclei in the cells of the root. Fiber stained according to the technique of Feulgen and mounted in tricresyl phosphate. Magnification × 500.

example, treatment of the sections with pepsin, sodium carbonate, or with a combination of both these reagents rendered the outline of individual cortical cells and their nuclei distinct (Fig. 4). Furthermore, when the cells were treated with Orange II * (a dye which readily stains wool) the cells became deep orange, but this central region was only lightly stained. Upon examination with crossed nicols, a dark, central, elongated area was nearly always detectable in the bright cell (Fig. 3, B). In other words, each birefringent cortical cell possesses a nonbirefringent nucleus. Finally after continued treatment with pepsin, many of the cortical cells were nearly eaten in two at the middle (Fig. 3, C), even though the cell is widest at this point. This suggested that the nucleus consists of a material which is more readily attacked by the enzyme than is the rest of the cell.

The structural details of the cortical cells were further investigated by dissecting them with the aid of a micromanipulator. Upon careful manipulation it was possible to insert two fine glass needles into a single cell and pull it apart. When this was done, it was found that the cell was composed of many fibrils (Fig. 5, A, B and C). When examined between crossed nicols the latter appeared to be birefringent. Small and large groups of fibrils were dissected from the cell, and in some cases all the fibrils were spread out in the form of a fan. By this technique it was possible to prove that the striated appearance of the cortical cells is due to the presence of fibrils and not merely to surface irregularities or diffraction phenomena.

3. Structure of the scale cells

As already described, the scales, unlike the cells of the cortex, were not appreciably affected by pepsin. They usually remained attached to each other in the form of tubes (Fig. 1, A, B, and C) corresponding to their arrangement in intact fibers, or at least in rather large groups, which furnished excellent material for a microscopic examination. The liberation of single scale cells was relatively infrequent, nor were additional ones readily released upon applying pressure to the cover glass. Although the scales stained poorly, the addition of a dye such as Orange II was helpful in showing their arrangement. It was clear after staining that the scales overlapped in a manner comparable to the arrangement of shingles on a roof (Fig. 6). Except for a few indistinct markings on the surface, individual scales showed little evidence of internal structure.

When handled with microneedles, groups of scales freed by the action of pepsin appeared to be rather pliable although the individual scale cells were not easily separated from each other. They could, nevertheless, be torn apart in such a way as to form chunks of scale material. In so doing there was no obvious fibrillar structure such as that shown by the cortical cells.

When the Feulgen test for nucleic acid (see section 4) was applied to untreated wool fibers, the scale cells of the shaft gave a negative test. Scales liberated from the fibers by various treatments were also examined in an effort to detect nuclei. Although structures superficially resembling nuclear bodies were observed occasionally in these cells, their presence could not be demonstrated clearly nor consistently.

* A 1.4 percent solution of Orange II at pH 1.5 was used.

Scales released by treatment with acids, alkalies, enzymes, or by mechanical scraping were examined between crossed nicols. In all cases, the scales, both before and after staining, showed practically no birefringence.

Additional information concerning the structure of the scales is contained in the section on the Allwörden reaction.

4. Differences between root and shaft

Since the cells of the root are alive and growing, whereas the cells of the shaft are dead, it is not surprising to find profound physical and chemical differences between these two regions of the fiber. Several of these differences were revealed when microchemical color tests were applied to wool fibers a short time after they had been carefully pulled from the back of a sheep so as to have the roots attached to the shaft.

These fibers were stained according to Feulgen's technique,[11, 12] which is considered to be specific for nucleic acid. A positive test is indicated by the red coloration obtained when a fuchsin-sulfurous acid solution is applied to the nucleus. Fibers which had been given this test showed a root which was stained deep red whereas the shaft remained colorless (Fig. 7). This difference could be detected even with the unaided eye. Upon mounting the stained fibers in a medium of higher refractive index and examining with a microscope, individual nuclei were observed (Fig. 8). At the base of the root the nuclei and cells were relatively large and more or less rounded. Farther from the base the nuclei and cells were elongated. In some cases the nuclei were very narrow and slit-like, although distinctly red. A little below the level where the fiber emerges from the skin there was a rather abrupt change in the reaction of the nuclei, that is, they gave a negative Feulgen test in the shaft. That this difference did not appear to be caused by poor penetration of the dye into the shaft was indicated by the fact that fibers from which the scales had been removed by mechanical treatment still failed to give a positive test.

In order to study further the changes which take place as the cells pass from the root to the shaft, longitudinal sections were made of pieces of sheepskin with fibers attached. The tissue was embedded in a mixture of paraffin and cellulose acetate[13] cut into sections according to the usual cytological procedure, and then stained either with hematoxylin or according to the method of Feulgen. The cells of the root had a somewhat roundish shape and a more or less granular appearance. The cells of the shaft, on the other hand, were elongated and distinctly fibrous. These facts are undoubtedly related to observations made with crossed nicols, which show that the shaft of the fiber is birefringent whereas the birefringence of the root is negligible. In agreement with the results obtained with single fibers, the nuclei in the cells of the root were found to give a positive reaction to Feulgen's test. Nuclei were observed in those cells of the root which gave rise to scales as well as in those which gave rise to cortical cells.

When a single fiber was mounted in dilute ammonium hydroxide and treated with sodium nitroprusside, a pink to red color was developed in the root, whereas the shaft of the fiber remained colorless (Fig. 9). The red coloration obtained with sodium nitroprusside indicates that at least some of the sulfur in the root is present in sulfhydryl form. This is in

agreement with the findings of previous investigators [14, 15, 16, 17, 18] who showed that the sulfhydryl-containing substance is limited to the living cellular parts of the epidermis and its appendages. In order to be sure that the difference in reaction between the root and shaft was not caused merely by a differential rate of penetration of the reagent, the scales were mechanically removed from a few fibers. The results with such fibers were in agreement with those obtained in the original test.

The biuret test for proteins, the Sakaguchi test for arginine, and the Millon and Pauly tests for tyrosine were also applied to single fibers. These tests did not reveal any differences between the root and shaft, except that the former gave a positive test more quickly.

The differences between the root and shaft may be summarized as follows:

Root	*Shaft*
Soft and easily crushed	Tough and horny
Cells roundish	Cells elongated
Positive test for nucleic acid	Negative test for nucleic acid
Nuclei stained with hematoxylin	Nuclei unstained with hematoxylin
Cytoplasm granular in appearance	Cells distinctly fibrous
Not birefringent	Birefringent
Positive test for sulfhydryl groups	Negative test for sulfhydryl groups
No Allwörden reaction with chlorine water	Many large Allwörden "sacs" *

5. The Allwörden reaction

When wool fibers are placed in chlorine water the so-called Allwörden reaction takes place.[19, 20] This treatment causes the formation of sacs on the surface of the fiber (Fig. 10, A and B). That the formation of these sacs is in some way associated with the scales has been suggested by many investigators.[5, 19, 20, 21, 22, 23] It is not clear, however, from a review of the literature, whether the sacs arise solely from the scales, or whether the latter are merely pushed out by the swelling of a layer of material which lies beneath them. Since this is pertinent to an understanding of the structure of the fibers, the reaction was investigated in detail.

Although sacs form quickly with saturated chlorine water, their formation is slowed down by the use of dilute solutions. Likewise, the reaction is retarded, or even completely inhibited, by certain types of damage to the fiber. The first evidence of sacs is the appearance on each scale of a small swelling, which gradually increases in size until the sac involves the entire scale surface. Incipient swelling did not appear to be confined to a particular part of the scale, such as base or tip. In a few cases two or more foci of swelling occurred in a single scale and were observed to flow together to form one large sac. It was also evident from the experiments that the size and shape of the sacs were associated with similar properties of the scales.

The sacs usually appeared optically empty. After certain treatments, however, particles showing Brownian movement were observed in them. As described by Kronacher and Lodemann,[3] these particles were especially numerous when fibers which had been stained with picric acid were placed in aqueous methylene blue subsequent to their treatment with chlorine

* Since the swellings are shown to be protein membranes filled with liquid, "sac" is believed to be a more appropriate descriptive term than "bubble," which is in widespread use in the literature.

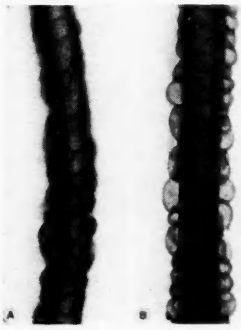

Fig. 10.

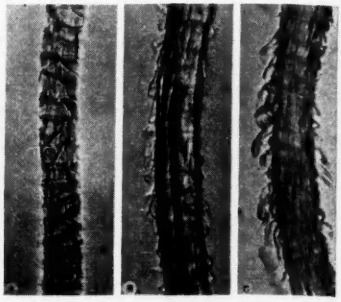

Fig. 12.

Fig. 11.

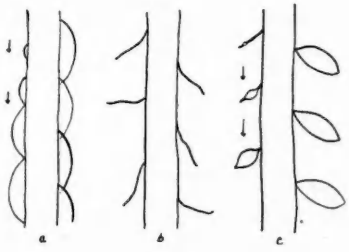

Fig. 13.

Fig. 13.—Diagram illustrating, in longitudinal view, the formation of sacs. A. The origin of sacs in intact fibers. B. The separation of scales upon treating intact fibers with sulfuric acid. C. The origin of sacs on single scales which have been separated by the treatment with acid. Arrows indicate an increase in size of the sacs.

Fig. 10.—Fibers treated with saturated chlorine water to give the Allwörden reaction. A. Surface view of a fiber after sac formation. B. Fiber in focus approximately midway between its upper and lower surfaces. Fibers stained with aqueous methylene blue. Magnification × 500.

Fig. 11.—The effect of alkali on Allwörden sacs. Single fiber treated with chlorine water, methylene blue, and then 1 percent sodium hydroxide, showing the collapsed sac membranes at the surface of the fiber. Magnification × 500.

Fig. 12.—Scales and their relation to the formation of Allwörden sacs. A. Fiber mounted in water and photographed in surface view to show the arrangement of the scales. B. Fiber treated with concentrated sulfuric acid to loosen scales. C. Fiber treated with sulfuric acid to loosen the scales, and then with chlorine water to form sacs. The photomicrograph shows several sacs in various stages of formation, each arising from an individual scale. Magnification × 450.

water. In agreement with the observations of Kronacher and Saxinger,[22] it was found that the thin membrane of a sac could be stroked with a needle of the micromanipulator without causing the sac to burst, but just as soon as the microneedle pierced the membrane the sac collapsed, leaving small bits of the membrane still attached to the fiber. Likewise the sacs collapsed after prolonged treatment with chlorine water, and after exposure to certain chemical agents, especially alkalies (Fig. 11). The sacs were stained by dyes, such as methylene blue and malachite green, and this treatment was helpful in studying their size and shape.

When cross sections about as thick as the length of the scales of wool fibers were treated with chlorine water, typical sacs were formed. The latter appeared to arise superficially on the surface of the scales. There was no swelling of the region just inside the scales, such as might have been expected if some part of the fiber in addition to the scales was directly involved in the formation of sacs. Although the results of this experiment, as well as some observations with intact single fibers, suggest that the scales alone give rise to sacs, this fact could not be demonstrated clearly by these techniques.

In untreated wool the scales are closely appressed to one another (Fig. 12, A). In carrying out some preliminary experiments during the course of this investigation, however, it was noted that certain chemical treatments loosened the scales and caused them to bend away from the fiber. For example, when wool fibers were placed in concentrated sulfuric acid for an hour or less, or in concentrated formic acid for several weeks, the scales were loosened in a way which resembled warped shingles on a roof (Fig. 12, B). After prolonged treatment with these acids, single scales, or small groups of scales, were completely separated from the fibers. Scales which had been loosened or liberated in this way were excellent for studying the origin of the sacs. After removal from the acid, the fibers were washed with distilled water and then placed in chlorine water. Sacs formed quickly, and in agreement with the conclusions of Müller,[6] it was evident that they came from the scales alone. It was clear, also, that the sacs were formed between the upper and lower surfaces of each individual scale cell. A small swelling first appeared somewhere in the scale, and then increased in size until the whole scale was swollen to resemble a little ellipsoidal bag (Fig. 12, C). Both the upper and lower surfaces of a sac appeared to be of approximately equal thickness. After their formation, the sacs on loose scales showed the same behavior to dyes and chemical reagents as the sacs on fibers which had not been treated with acids. Where the scales were loosened from each other but not bent away from the fiber, the formation of sacs aided in the further separation of the scales. Sometimes sacs were formed on completely isolated scales; at other times where only fragments of single scales were treated with chlorine, sacs were not formed although the two layers of the scale were seen to separate. Apparently in the latter instance true sacs could not form because of the torn edges of the scales. The relationship between the formation of sacs in untreated and in acid-treated fibers is shown diagrammatically in Fig. 13.

Chlorine water caused the formation of sacs on all parts of a wool fiber except the root (Fig. 14). Tests on hairs from more than a score of common and rare animals were, likewise, found to give the Allwörden reaction.

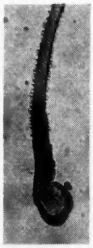

Fig. 14.

Fig. 14.—Fiber showing root and part of the shaft, after treatment with chlorine water. Many sacs arise in the shaft but none in the root. Magnification × 120.

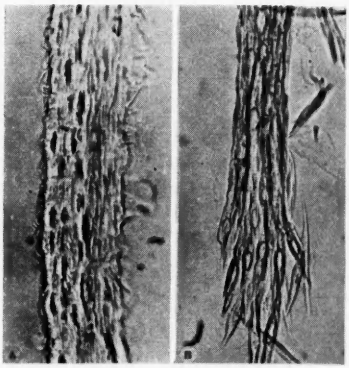

Fig. 15.

Fig. 15.—Fibers showing swellings in the cortex after treatment with acid and chlorine water. A. Wool fiber after 2 hours in concentrated sulfuric acid followed by treatment with chlorine water. B. Wool fiber after 14 months in concentrated formic acid followed by treatment with chlorine water. Similar results were obtained with fibers that had been boiled in the acid for about 4 hours. Magnification × 450.

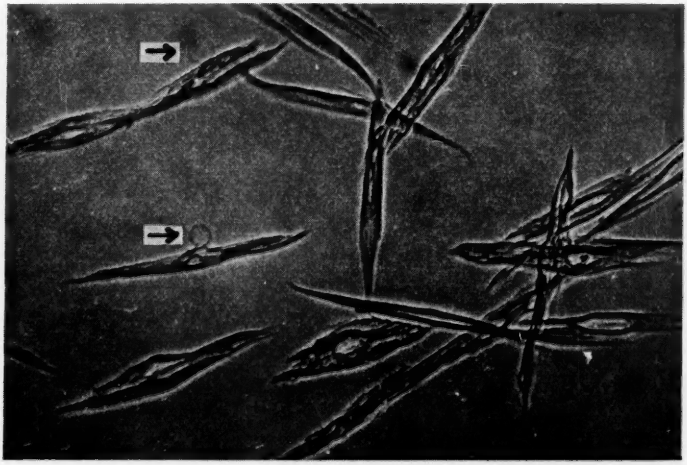

Fig. 16.

Fig. 16.—Individual cortical cells showing swollen nuclei after treatment with chlorine water. The cells were released by the prolonged action of concentrated formic acid, and then, after washing in distilled water, treated with chlorine. Arrows indicate additional swellings which sometimes arise from the nucleus. Magnification × 420.

In order to study further the conditions necessary for the formation of Allwörden sacs on the scales, untreated wool was placed in a 0.6-percent solution of sodium carbonate at 50° C. At various intervals thereafter, samples of the wool were removed, washed in acid and in water, and finally placed in chlorine water. The number, size, and rapidity of formation of the sacs was observed microscopically. It was found that sac formation was retarded with increasing length of alkali treatment. Mark [24] has similarly shown that the number of sacs formed on a fiber by chlorine water was decreased as the concentration of the carbonate and the temperature at which the reaction was carried out were increased. In the present investigation, chemical analysis of the fibers showed that as the cystine content of the fibers decreased, because of the action of the carbonate, sac formation was retarded. Similarly, samples of wool which were degraded by photochemical reactions showed poor sac formation. The extent of the sac formation varied with the duration of the irradiation. Samples of wool degraded in this way also had appreciably reduced cystine contents.[25, 26] The Allwörden reaction was also tried on samples of wool in which the mode of linkage of the sulfur had been altered by treatments such as reduction and alkylation. In all cases the sacs were formed more quickly when the cystine content was high, whereas the formation of sacs did not occur when the cystine content was lowered sufficiently. While not all of the above chemical treatments are specific for cystine in wool, it is significant, nevertheless, that samples of wool with low cystine contents fail to give the Allwörden reaction. The results suggest that the formation of sacs is dependent on the specific reaction of chlorine with unaltered disulfide groups of the cystine in the scales of the fiber. That chlorine can react with cystine has already been demonstrated.[27] A possible mechanism is that the disulfide linkages are split and oxidized to strongly acid groups such as perhaps sulfonic acid groups. An osmotic type of swelling could then take place to form the sacs noted. Further evidence favoring this view is obtained when concentrated salt solutions are added to the fibers after the reaction with the chlorine. Under these conditions the sacs contract.

It was noted, during the course of the above experiments with acid-treated wool, that when the scales gave rise to typical sacs, localized swellings often appeared in the cortex (Fig. 15, A and B). In order to study this phenomenon further, wool fibers were treated with acid for longer periods in order not only to loosen the scales but to release individual cortical cells as well. Fibers which had been placed in concentrated sulfuric acid at room temperature for 1 to 2 hours, or in boiling concentrated formic acid for about 6 hours, were found to be suitable for these experiments. Individual cortical cells released by these treatments showed distinct signs of swelling when placed in chloride water. It was obvious, moreover, that the swelling in each cell was confined principally to the nucleus (Fig. 15, B and 16). In some cases additional swellings appeared to arise as buds from the swollen nucleus (Fig. 16). Swollen nuclei were not observed in fibers which had been treated with alkali or other reagents which prevent the Allwörden reaction. Although the foregoing observations suggest that the typical Allwörden reaction of the scales and the swelling cortical nuclei may be related phenomena, additional experiments pointed to dissimilarities between the two. In the presence of concentrated salt solutions, for ex-

ample, the scale sacs became flaccid, and upon replacing the salt solution with water they regained their former turgidity; the nuclear swellings on the other hand failed to react in this way. Furthermore, a gentle prick with the tip of a microneedle was sufficient to bring about the collapse of scale sacs, whereas this did not occur when nuclear swellings were punctured.

IV. References

1. W. V. Nathusius, Das Wollhaar des Schafes, Berlin, 1866.
2. W. McMurtrie, Wool and Other Animal Fibers (Government Printing Office, Washington, 1886).
3. C. Kronacher and G. Lodemann, Technik der Haar und Wolleuntersuchung, Berlin, 1930.
4. W. von Bergen, American Wool Handbook, American Wool Handbook Publishing Co., New York, 1938.
5. H. Reumuth, *Klepzig's Textil-Zeitschrift 21*, 352 and *34*, 495 (1939).
6. C. Müller, Zeitschr. f. Zellforschung u. Mikroskopische Anatomie, A, *29*, 1 (1939).
7. W. B. Geiger, W. I. Patterson, L. R. Mizell and M. Harris. Publication in preparation.
8. G. L. Royer and H. E. Millson, *Am. Dyestuff Reptr. 29*, 697 (1940).
9. J. I. Hardy, U. S. Dept. of Agriculture Circular 378 (1935).
10. A. R. Walther, *Landw. Jahrb. 55*, 531 (1920–21).
11. R. Feulgen and H. Rosenbeck, *Zeitschr. f. Physicalische Chemie 135*, 203 (1924).
12. C. E. McClung, Handbook of Microscopical Technique (Hoeber, New York and London, 1939).
13. C. M. Barlow, *Journ. Text. Inst. 29*, T111 (1938).
14. E. Buffa, *J. Physiol. Path. Gen. 6*, 645 (1904).
15. E. Walker, *Jour. of Physiol. 59*, 32 (1924).
16. Ibid., *Biochem. Journ. 19*, 1085 (1925).
17. G. H. Perceval and C. P. Stewart, *Brit. Journ. Dermatology and Syphilis, 42*, 215 (1930).
18. P. Wels, *Archiv. f. experimentelle Path. u. Pharmak., 188*, 265 (1938).
19. v. Allwörden, Studien über Einwirkung von Chlor auf Schaffwolle. Diss. Berlin (1913).
20. v. Allwörden, *Zeitschr. angen. Chem. 29*, 77 (1916).
21. P. Krais and P. Waenting, *Zeitschr. f. angen. Chem.*, 33 (1920).
22. C. Kronacher and G. Saxinger, *Zeitschr, f. Tierzüchtung u. züchtungsbiol. 4*, 30 (1925) and *5*, 3 (1926).
23. W. Spöttel, *Melliand Textilber. 6*, 605 (1925).
24. H. Mark, Einzeldarst a.d. Kaiser-Wilhelms Institut f. Faserstoffchem. 1 (1925).
25. H. A. Rutherford and M. Harris, *Journ. Res. NBS 23*, 597 (1939), RP1255.
26. M. Harris and A. L. Smith, *Journ. Res. NBS 20*, 563 (1938).
27. M. Harris and A. L. Smith, *Journ. Res. NBS 17*, 577 (1936) RP928.

Oxidation of Wool Keratin by Potassium Permanganate

By MILDRED BARR AND RACHEL EDGAR *

Abstract

The degradation of wool by fifty volumes of 0.0100 to 0.0400 M potassium permanganate, by fifty volumes of 0.0100 to 0.0600 M potassium permanganate, 0.1800 N as to sulfuric acid, and by 62.5, 75.0, 87.5, and 100 volumes of 0.0200 M potassium permanganate, both aqueous and acidic, in ten hours at 40 ± 0.1° C. has been measured by the weight, nitrogen, total sulfur, sulfate sulfur, and wet strength of the residual wool.

Percentage losses in weight, nitrogen, and non-sulfate sulfur have been shown very similar in fifty-volume baths of either aqueous or acidic permanganate in the same molarity.

With increasing volume of 0.0200 M potassium permanganate, loss of nitrogen by wool has been shown greater in acidic than in aqueous solutions.

In no case did the wool's sulfate sulfur increase although part of its original sulfate sulfur dissolved in acid permanganate.

Wet strength of wool has been shown to decrease more rapidly than weight, nitrogen, or non-sulfate sulfur with increasing molarity or volume of permanganate and more rapidly in aqueous than in acidic permanganate.

Introduction

WANKLYN and Cooper in 1879 reported that oxidation by potassium permanganate of wool dissolved in potassium hydroxide yielded carbon dioxide, oxalic acid, and cyano-propionic acid.[45] Lisitzuin has described digestion in two per cent potassium permanganate as converting nine per cent of hair's sulfur to sulfuric acid, 2.5 per cent to oxykeratin-sulfonic acid, and 88.5 per cent to *dl*-cysteic acid.[25, 23]

Solutions of potassium permanganate, aqueous and acidic, 0.003 to 0.5 per cent potassium permanganate and 0.01 to 0.04 gram of permanganate per gram of wool, have been recommended for the bleaching of feathers,[16] fur,[22] mohair [18] and wool (see references 15, 34, 14, 5, 1, 40, 30, 17, 31, 24, 39, 3, 19, 27, 20, 12, 21, 11) though frequently with cautions against resulting damage and harsh handle and scroop. Lowe, Lloyd, and Smith have bleached wool for ten successive one-minute periods at 30° C. in solutions of 0.5 per cent and one per cent permanganate, 1.5 per cent as to acetic

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acid, freed the wool from oxides of manganese by hydrogen peroxide in a solution of acetic acid, and tested the residual wool for solubility in alkali by the method of Harris and Smith; they concluded that the slightly greater effect on wool of one per cent, as compared with 0.5 per cent, permanganate was of no practical importance.[28]

Seven per cent permanganate has been proposed as a pre-treatment for the dyeing and printing of hair and wool[35, 36, 23, 7] and in other concentrations permanganate has been used for the production of Manganese Brown on hair and wool.[4, 9, 20]

Treatment with permanganate has been described both as causing wool to lose its felting power[35, 36, 23] and as bringing about the felting of wool.[29, 41, 37, 38, 33]

Experimental Procedure

Preparation of wool

Plain-woven white wool batiste was boiled one hour in 100 volumes of water, dried at room temperature, cut for analysis, and extracted continuously with diethyl ether for eighteen hours in a modified Soxhlet extractor. This procedure yielded a keratin of 0.01 ± 0.01 per cent ash, 0.93 ± 0.1 per cent sulfate sulfur, no sulfite sulfur, and a wet strength of ten pounds per inch.

Treatment with permanganate

A five-gram sample of this prepared wool was dried to constant weight at 105 to 110° C. before immersion in water or dilute permanganate for ten hours in a stoppered flask at 40 ± 0.1° C. in a water bath. Fifty-volume baths were used with water and 0.0100, 0.0150, 0.0200, 0.0300, and 0.0400 *M* potassium permanganate and with these molarities as well as 0.0500 and 0.0600 *M* potassium permanganate made 0.1800 *N* as to sulfuric acid. In the case of 0.0200 *M* potassium permanganate, both aqueous and acidic, the wool was also treated with 62.5, 75, 87.5, and 100 volumes of oxidant. The wool was freed from oxides of manganese by 0.5 per cent sodium hydrogen sulfite in two hours at room temperature and washed with water until the rinse did not decolorize permanganate. Ten residual inch strips of wool were at once tested for wet strength[2] but the five-gram samples were either dried at room temperature before determination of their nitrogen and sulfate sulfur or dried until constant at 105 to 110° C. before estimation of their total sulfur. Each value for residual weight is the mean of at least three parallel determinations.

The potassium permanganate was prepared by dissolving the chemically pure reagent in boiled distilled water, allowing this solution to stand for several days in a tightly stoppered brown bottle, and filtering it through acid-digested asbestos. Each solution was standardized against sodium oxalate in a hot solution of sulfuric acid.[44b]

The solutions of sodium hydrogen sulfite were prepared by dissolving the calculated amount of chemically pure reagent in distilled water and were standardized by titration of the iodine liberated from an acidified solution of potassium iodide by 25 milliliters of 0.1000 *N* potassium permanganate.[42]

Table 1. Effect of fifty volumes of sodium hydrogen sulfite in ten hours at 40° C. on the weight, ash, nitrogen, sulfur, and wet strength of wool.

Sodium hydrogen sulfite *normality*	Residual Wool						
	Weight *percentage of wool*	Ash *percentage of wool*	Nitrogen *percentage of wool*	Total sulfur *percentage of wool*	Sulfate sulfur *percentage of wool*	Sulfite sulfur † *percentage of wool*	Breaking strength of wet warp *pounds per inch*
0.0000	98.9 (0.1*)	0.01 (0.01)	16.11 (0.03)	4.68 (0.01)	0.93 (0.01)	0.20 (0.00)	10 (0)
0.4768							9 (1)
0.9536							8 (1)
1.4302							8 (1)
1.9050	99.0 (0.1)	0.12 (0.01)	16.26 (0.01)	4.72 (0.01)	0.86 (0.01)	0.31 (0.02)	5 (1)

* Mean deviations are within parentheses.
† Compared with 0.25 ± 0.01 per cent sulfite sulfur in a Cotswold wool fiber.

The effect of sodium hydrogen sulfite on the wool was investigated by immersing five grams of it in fifty volumes of 1.9050 *N* sodium hydrogen sulfite in a stoppered flask for ten hours at 40 ± 0.1° C. in a water bath and washing the residual wool until the rinse no longer decolorized permanganate. From the data of Table 1 it was assumed that two hours in 0.5 per cent or 0.0961 *N* sodium hydrogen sulfite at room temperature had no measurable effect on the composition or strength of the wool.

Ash

A five-gram sample of wool was ignited to constant weight in an electric muffle furnace at dull red heat. The values reported are the means of at least two determinations based on the original wool dried to constant weight at 105 to 110° C.

Total nitrogen

Each value for nitrogen is the mean of four parallel determinations with five-gram samples by the Kjeldahl method,[44a] corrected by blank determinations and based on the weight of the original wool dried until constant at 105 to 110° C.

Total sulfur

By digestion on a steam plate a five-gram sample of wool was dissolved in 100 milliliters of a solution one part concentrated nitric acid and two parts water. After addition of 100 milliliters of Benedict-Denis reagent [8] and evaporation to dryness the residue was heated to dull redness for ten minutes, dissolved in 100 milliliters of ten per cent hydrochloric acid, and filtered; this filtrate was heated to boiling and its sulfur precipitated as barium sulfate by addition of 25 milliliters of ten per cent barium chloride. After fifteen hours the precipitate was filtered into a Gooch crucible, washed free of chloride, and ignited to constant weight at dull red heat in an electric muffle furnace. Each value for total sulfur is the mean of at least three parallel determinations, corrected by blank determinations and based on the weight of the original wool at 105 to 110° C.

Sulfate sulfur

A five-gram sample of wool was prepared for precipitation of its sulfate sulfur by dissolving it in fifty milliliters of thirty per cent hydrochloric acid on a boiling water bath and cooling this solution and diluting it with an equal volume of water before filtration.[32] Each value is the mean of at least two parallel determinations, corrected by blank determinations and based on the weight of the original wool dried at 105 to 110° C.

Sulfite sulfur

Five grams of wool were put into a mixture of sixty milliliters of dissolved stannous chloride and ten milliliters of ten per cent barium chloride in a balloon flask fitted with a delivery tube dipping into a mixture of

Table 2. Effect of fifty volumes of potassium permanganate in ten hours at 40° C. on the weight, nitrogen, sulfur, and wet strength of wool.

Table 2. Effect of fifty volumes of potassium permanganate in ten hours at 40° C. on the weight, nitrogen, sulfur, and wet strength of wool.

Potassium permanganate		Residual wool					
		Weight		Total nitrogen		Total sulfur	
molarity	*gram per gram of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*
0.0000	0.0000	98.9 (0.1*)		16.11 (0.03)		4.68 (0.01)	
0.0100	0.0790	96.7 (0.3)	96.7 (0.1)	15.70 (0.04)	15.76 (0.02)	4.54 (0.00)	4.68 (0.01)
0.0150	0.1185						
0.0200	0.1580	92.3 (0.3)	91.3 (0.8)	14.94 (0.04)	15.02 (0.02)	4.38 (0.01)	4.02 (0.01)
0.0300	0.2370	83.8 (1.4)	85.1 (0.4)	13.98 (0.01)	13.91 (0.02)	4.26 (0.03)	3.76 (0.02)
0.0400	0.3161	76.3 (0.6)	77.5 (0.9)	12.87 (0.02)	12.91 (0.02)	3.84 (0.02)	3.38 (0.02)
0.0500	0.3951		72.5 (0.7)		11.90 (0.06)		3.14 (0.02)
0.0600	0.4741		63.5 (0.5)		10.92 (0.14)		2.79 (0.03)

* Mean deviations are within parentheses.

Potassium permanganate	Residual wool					
	Sulfate sulfur		Non-sulfate sulfur		Breaking strength of wet warp	
molarity	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *pounds per inch*	Acidic *pounds per inch*
0.0000	0.93 (0.01)		3.75		10 (0)	
0.0100	0.92 (0.01)	0.90 (0.02)	3.62	3.78	7 (1)	10 (1)
0.0150					4 (1)	6 (0)
0.0200	0.81 (0.02)	0.44 (0.02)	3.57	3.58	3 (1)	5 (2)
0.0300	0.90 (0.02)	0.46 (0.05)	3.36	3.30	<1	3 (0)
0.0400	0.90 (0.02)	0.40 (0.00)	2.94	2.98	<1	2 (1)
0.0500		0.37 (0.01)		2.77	<1	1 (1)
0.0600		0.33 (0.04)		2.46	<1	<1

Table 3. Effect of volume of 0.02 *M* potassium permanganate in ten hours at 40° C. on the weight, nitrogen, sulfur, and wet strength of wool.

Potassium permanganate		Residual wool					
		Weight		Total nitrogen		Total sulfur	
milliliters 0.02 M $KMnO_4$ per gram of wool	*gram per gram of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*
50.00	0.1580	92.3 (0.3*)	91.3 (0.8)	14.94 (0.04)	15.02 (0.02)	4.38 (0.01)	4.02 (0.01)
62.50	0.1975	88.5 (0.3)	87.6 (0.5)	14.43 (0.01)	14.07 (0.01)	4.30 (0.03)	3.86 (0.04)
75.00	0.2370	84.4 (0.1)	82.7 (0.6)	13.99 (0.03)	13.47 (0.02)	4.00 (0.04)	3.58 (0.03)
87.50	0.2766	80.5 (0.7)	79.3 (0.4)	13.45 (0.02)	13.15 (0.01)	3.90 (0.04)	3.54 (0.04)
100.00	0.3161	75.5 (0.4)	78.1 (0.9)	12.88 (0.08)	12.64 (0.02)	3.82 (0.03)	3.52 (0.04)

* Mean deviations are with parentheses.

Potassium permanganate	Residual wool					
	Sulfate sulfur		Non-sulfate sulfur		Breaking strength of wet warp	
milliliters 0.02 M $KMnO_4$ per gram of wool	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *percentage of wool*	Acidic *percentage of wool*	Aqueous *pounds per inch*	Acidic *pounds per inch*
50.00	0.81 (0.02)	0.44 (0.02)	3.57	3.58	3 (1)	5 (2)
62.50	0.90 (0.04)	0.56 (0.04)	3.40	3.30	<1	4 (0)
75.00	0.87 (0.04)	0.47 (0.03)	3.13	3.11	<1	3 (1)
87.50	0.98 (0.02)	0.50 (0.01)	2.92	3.04	<1	<1
100.00	0.94 (0.02)	0.42 (0.02)	2.88	3.10	<1	<1

100 milliliters of ten per cent potassium hydroxide and 100 milliliters of 0.1 *M* iodine. After the contents of the balloon flask were vigorously boiled for thirty minutes the alkaline solution of iodine was boiled for a few minutes, filtered, acidified with hydrochloric acid, concentrated to a small volume, and again filtered before precipitation of the sulfur as barium sulfate.[13] Each value is the mean of at least two parallel deterinations, corrected by blank determinations and based on the weight of the original wool dried at 105 to 110° C.

Discussion of Results

The wet strength of this wool (Table 2) is shown to decrease much more rapidly with increasing molarity of aqueous permanganate (where the greatest alkalinity is 0.0400 *N*) than of acidic permanganate; the total nitrogen and the non-sulfate sulfur of the wool are shown to decrease less rapidly than its wet strength, but each to the same extent in aqueous as in acidic permanganate.

Table 3 shows that wool treated with increasing volumes of 0.0200 *M* potassium permanganate, 0.1800 *N* as to sulfuric acid, not only decreased less rapidly in strength and lost more sulfate sulfur but that it also lost more nitrogen than wool treated with aqueous permanganate.

Consideration of the effects of the four solutions containing 0.2370 gram of potassium permanganate per gram of wool shows that a greater loss of the wool's nitrogen occurs in the greater volume of the lower molarity of acidic permanganate, that the wet strengths are the same, but that a greater loss of the wool's non-sulfate sulfur occurs in the greater volume of the lower molarity of either aqueous or acidic permanganate. Similar consideration of the effects of the solution containing 0.3161 gram of potassium permanganate per gram of wool is doubtless of little meaning in case of wool treated with aqueous permanganate; the greater volume of the lower molarity of acid permanganate yielded a wool lower both in nitrogen and in wet strength.

Although residual wools from treatment with other oxidants have been described as containing sulfate equivalent to part of their original sulfur,[6, 42] in no case in this study was the sulfate sulfur of wool increased by potassium permanganate. The residual ash of wool was raised to 0.48 per cent by the treatment with acidic permanganate at 0.0600 *M*.

Losses of nitrogen and non-sulfate sulfur, computed as percentages of these constituents in the original wool, are so similar as to indicate solution of the wool fiber at its surface rather than elimination of portions containing different ratios of nitrogen to sulfur.

Although aqueous solutions of potassium permanganate are more commonly used in the processing of wool, acidic solutions of the same molarity have been shown preferable and specification of volume as well as concentration of oxidant essential.

Acknowledgment

We wish to thank Miss Maurine Jones for determination of the ash, sulfite sulfur, and wet strength of the wool treated with sodium hydrogen sulfite.

References

1. Albert, W. *Deut. Färber-Ztg. 57*, 61 (1921); *C. A. 15*, 1078 (1921).
2. "A.S.T.M. Standards on Textile Materials," p. 4. Philadelphia: American Society for Testing Materials, 1933.
3. Anon. *Tiba 11*, 17, 19, 21, 23 (1933).
4. Bachstez, M. *Color Trade J. 11*, 90–2, 191–2, 270–3 (1922).
5. Berwick. *Textile World 51*, 1555 (1916).
6. Blumenthal, D., and H. T. Clarke. *J. Biol. Chem. 110*, 343–9 (1935).
7. Booth, L. W. *Dyer 74*, 161–2 (1935)
8. Denis, W. *J. Biol. Chem. 8*, 401–3 (1910).
9. Franz, E. U. S. Patent 2, 198,994 (Apr. 30, 1940).
10. Franz, E., and Kammgarnspinnerei, Stöhr und Co. A.-G. Brit. Patent 501,643 (Feb. 28, 1939).
11. Fulton, G. *Laundry Dry Cleaning J. Can. 19*, No. 6, 20, 26 (1939).
12. Goldsmid, P. *Papier 39*, 47–8, 51, 53 (1936).
13. Goodall, F. L. *J. Soc. Dyers Colourists 50*, 10–3 (1934).
14. Graham, T., and F. Cope. Brit. Patent 8851 (Apr. 18, 1904).
15. Grothe, H. *Dinglers polytech. J. 195*, 360–4 (1870).
16. Grove-Palmer, F. *Textile Colorist 52*, 606–7 (1930).
17. Guernsey, F. H. *Am. Dyestuff Reptr. 13*, 325–6 (1924).
18. Hillman, B. S. *Dyer 70*, 543–4 (1933).
19. Holmes, J. F. *Textile Colorist 55*, 250, 276 (1933).
20. *Ibid.* 314–7 (1936).
21. Hünlich, R. *Monatschr. Textil-Ind. 53*, 133–5 (1938); *C. A. 32*, 6872 (1938).
22. Issakovitch, A. *Halle aux cuirs 1938*, 160–3, 187–91; *C. A. 32*, 9543 (1938).
23. Kammerer, F. H. Brit. Patent 5612 (Mar. 8, 1907).
24. Krais, P. *J. Textile Inst. 23*, P144–6 (1932).
25. Lisitzuin, T. *Biochem. Bull. 4*, 18–23 (1915).
26. Ibid. *Z. physiol. Chem. 173*, 309–11 (1928).
27. Loescher, M. *Deut. Wollen-Gewerbe 66*, 713–4 (1934); *C. A. 29*, 8343 (1935).
28. Lowe, C. S., A. C. Lloyd, and A. C. Smith. *Am. Dyestuff Reptr. 30*, 81–4, 106 (1941).
29. Martin, J. H. French Patent 634,662 (May 18, 1929).
30. Matthews, J. M. "Bleaching and Related Processes," pp. 145–7. New York: The Chemical Catalog Company, Inc., 1921.
31. Ibid. "The Textile Fibers," 4th ed., p. 159. New York: John Wiley and Sons, Inc., 1924.
32. Mease, R. T. *J. Research N. B. S. 13*, 617–23 (1934).
33. Mercier, W. C. U. S. Patent 2,148,031 (Feb. 21, 1939).
34. Mothay, T. du. *Jahresber. phys. Ver. zu Frankfurt a. Main 1877–8*, 19; *Chem. Zentr. 1879*, 752.
35. Mullerus, J. *Chem.-Ztg. 15*, 1674–5 (1891).
36. Ibid. *Färber-Ztg. 1*, 221–2, 237–40 (1891–2).
37. No-Mercury Felt Corporation. Brit. Patent 499,670 (Aug. 4, 1937).
38. Ibid. French Patent 824,812 (Feb. 17, 1938).

39. Rinoldi, L. *Boll. laniera 46,* 683–5 (1932).

40. Rot, E. *Deut. Färber-Ztg. 57,* 227–8 (1921); *C. A. 15,* 1998 (1921).

41. Sartakoff, J. D. U. S. Patent 2,070,927 (Feb. 16, 1937).

42. Scott, W. W. "Standard Methods of Chemical Analysis," 4th ed. p. 512. New York: D. Van Nostrand Company, 1925.

43. Smith, A. and M. Harris. *Am. Dyestuff Reptr. 25,* P383–5 (1936).

44. Treadwell, F. P. and W. T Hall. "Analytical Chemistry. Vol. II. Quantitative Analysis," 4th ed. (a) pp. 63–4; (b) p. 597. New York: John Wiley and Sons, Inc., 1911.

45. Wanklyn, J. A. and W. J. Cooper. *Phil. Mag.* [*5*] *7,* 356–65 (1879).

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I. Fibers (Synthetic and Natural) and Fiber Analysis

The Application of Viscosity Data to the Determination of the Shape of Protein Molecules in Solution. J. M. Burgers. *Proc. Konink. Nederlandsche Akad. Wet.*, 1940, V. 43, No. 5, P. 645–52; abs. in *Eastman Kodak Abstract Bull.*, 1941, Feb., P. 67; March, P. 114.

(See *Monthly Abst. Bull.*, August 1940, V. 26, P. 439.) The theoretical viscosity treatment of Huggins (*Monthly Abst. Bull.*, 1939, V. 25, P. 558; 1940, V. 26, P. 343) is extended to systems of four spheres at the corners of a square. Experimental data for solutions of protein molecules are discussed in the light of the various theoretical equations. The assumption that the molecules have the shape of ellipsoids of revolution is not a good approximation. Other alternative shapes are considered, but no thoroughly satisfactory conclusions are reached. (S)

Comparative Observations on the Swelling of Jute Fiber. 2. Specific Gravity and Swelling. W. G. Macmillan and M. K. Sen. *J. T. I.*, March 1941, V. 32, P. T45–T56.

The true and apparent specific gravities of dry jute fibers have been found to be 1.436 and 1.559, respectively. The volume swelling of fibers calculated from the specific gravity is 45%. Measurements on cross-sections as well as on diameters indicate that swelling diminishes with increase of area or diameter of fibers. The effect of temperature and humidity on dry weights of fibers has been investigated. (C)

II. Yarns and Fabrics

Cellulose Acetate Rayons: Properties and Uses. H. DeWitt Smith. *Ind. Eng. Chem.*, 1940, V. 32, P. 1555–59; abs. in *J. T. I.*, March, 1941, V. 32, P. A116.

A general account is given of the production, properties and uses of the various types of cellulose acetate rayon and staple fiber and of recent progress in the acetate rayon industry. (C)

Crepe-de-Chine Hosiery Yarn. *Text. Wld.*, April 1941, V. 91, P. 94.

The article describing the construction and properties of this new yarn was written for *Textile World* by one of the men who was instrumental in its development. (C)

Development in Wool Combing. A. Geoffrey Peel. *Text. Recdr.*, April 1941, V. 58, P. 23–4; *Text. Mfr.*, April 1941, V. 67, P. 123–4.

Trends of progress in wool-combing include the use of shorter wools, more burry wools, production of dry-combed tops and many mechanical and other refinements. (C)

Fabrics: Value of Individualized Shrinkage Tests. *Text. Mercury and Argus*, 1940, V. 103, P. 541; abs. in *J. T. I.*, Feb., 1941, V. 32, P. A68.

It is pointed out that cloth in the unshrunk state is a mass of unbalanced tensions resulting from the effects of spinning, weaving and finishing processes and that differing fabric structures have varying degrees of unbalance. The normal processes of weaving and finishing tend frequently to create greater tensions in warp than in weft, and as a general rule the warp threads have a greater unbalance to correct. In a series of washing tests conducted over ten launderings on a variety of fabrics, poplins, drills, jeans, twills, cellulars, etc., it was discovered that although in all cases the cloth at the end of the tenth wash showed greater warp shrinkage than in the first wash, seven out of sixteen fabrics showed less weft shrinkage at the tenth than in the first. These results show the intricate and varied nature of shrinkage and the need for studying warp and weft shrinkage separately and for treating individual groups of cotton fabrics differently according to their needs and behavior. (C)

The Future Prospects of the Tricot Machine. Otto Engelhard. *Rayon Text Mo.*, April 1941, V. 22, P. 75–6. (C)

How Nylon Yarn is Sized in Preparation for Knitting. Victor A. Schiffer. *Rayon Text Mo.*, 1941, April, V. 22, P. 73–4; May, V. 22, P. 49–50; June, V. 22, P. 58–9.

The author reveals the exact sizing ingredients, the application of the size, the control and testing of the amount, and all details of sizing and throwing nylon yarn in preparation to knitting it into full fashioned hosiery, as developed and recommended by du Pont. (C)

Knitting Nylon Hosiery. Milton M. Abrams. *Text. Wld.*, April 1941, V. 91, P. 68. (C)

III. Chemical and Other Processing (Not Otherwise Classified)

An Analysis of the Split Bath Method of Dyeing Silk Hosiery. *Am. Dye. Reptr.*, 1941, V. 30, No. 8, P. P211–P214. (C)

Color: Control. T. Vickerstaff. *J. Soc. Dyers & Col.*, 1940, V. 56, P. 461–472; abs. in *J. T. I.*, Feb. 1941, V. 32, P. A56.

The difficulty of measuring and specifying colors is discussed and the principles underlying the measurement of color by spectrophotometers and trichromatic colorimeters are briefly explained. The general design of spectrophotometers is outlined and the use of such instruments for estimating the strength of dyes, the amount of color on dyed cellulose acetate rayon, the identification of dyes and other purposes is discussed. Trichromatic colorimeters are also discussed and examples of their uses in, e. g., color matching, and determinations of washing-fastness, light-fastness, and the actual quantity of dye present on a fabric, are described. Limitations of both types of instruments are pointed out. The possibility of determining, from the trichromatic values of a given pattern, the necessary dyes and their amounts required to produce a matching is discussed. A report is given of a discussion of the paper. (C)

Color Fastness on Spun Rayons. Henry F. Herrmann. *Am. Dye. Rptr.*, 1941, V. 30, No. 6, P. 135–37, 161–62. (C)

A Comparison of End-Group Determination and Viscosity of Cellulose. K. Hess and E. Steurer. *Ber. deut. chem. Ges.*, 1940, V. 73, No. 6, P. 669B–76B; abs. in *Eastman Kodak Abs. Bull.*, April 1941, P. 153.

A comparison of the degree of polymerization of cellulose as determined by Haworth's (*Ibid.*, 1932, V. 65, P. 60) end-group method and by Staudinger's (*Ibid.*, 1930, V. 63, P. 2331; 1934, V. 67, P. 84) viscosity method shows a progressively greater divergence the longer the chain length. (S)

Dermatitis from Textile Finishes. Walter M. Scott. *Cotton*, April 1941, V. 105, P. 71–2.

A commonsense view of the present situation. (C)

The Effect of Acid Baths in the Presence of Eulan New on the Chemical and Physical Properties of Wool. H. Rath, H. J. Künstler and Fritz Siems. *Klepzig's Textil-Z.*, V. 43, P. 403–6 (1940); abs. in *C. A.*, V. 34, Col. 8287.

The addn. of Eulan New to the dyeing bath improves the properties of wool. The Puly-Binz diazo reaction and the Sieber reaction indicate practically no change of dye-absorption power. However, in wool that has been treated in the presence of relatively large amts. of H_2SO_4 these tests indicate a slight damage of the wool treated with Eulan. (C)

Fatty Acid Derivatives and Their Importance in Regard to Softening and Color Fixation, with Special Reference to Sapamines. T. A. Forster. *J. Soc. Dyers Col.*, Dec. 1940, V. 56, P. 497. (C)

FUNCTIONS AND REACTIONS OF PHENOLS IN HAIR DYES. H. E. Cox. *Analyst*, 1940, V. 65, P. 393–98; abs. in *J. Soc. Dyers Col.*, Dec. 1940, V. 56, P. 527.

It is concluded that the functions of phenols in hair dye mixtures are as follows—(a) They promote the formation of fast colors, particularly brown shades, (b) prevent the formation of Bandrowski's base, (c) give a better color for the same amount of diamine, (d) promote the formation of *o*-indophenols and oxazones in the fiber, and (e) the trihydric phenols retard the oxidation of the diamines, form complexes with the base and promote the formation of light brown colors. These results are brought about mainly by the formation of *o*-quinonoid indophenols which are further oxidized to oxazones. (C)

GAS FADING OF DYED ACETATE DRESS FABRICS. *Canadian Text. J.*, 1940, V. 57, No. 20, P. 30, 32.

The technical problem of gas fading of dyed acetate materials in relation to testing and use of suitable dyestuffs, use of anti-fume finishes, and precautions to prevent fading during cloth and garment storage. (C)

HIGH MOLECULAR WEIGHT CHEMICALS IN FINISHING. II. Resins Formed by Condensation. *Text. Recdr.*, April 1941, V. 58, P. 29–31. (C)

HOSIERY DYEING. C. Harrell Asbury. *Am. Dye. Rptr.*, 1941, V. 30, No. 8, P. 204, P205, P210.

Discusses developed, sulfur, napthol and vat dyes and their application. (C)

HOW DO ALKALIES AFFECT THE WOOL FIBER? Willy Hacker. *Klepzig's Textil-Z.*, V. 43, P. 465–7 (1940); abs. in *C. A.*, V. 34, Col. 8289.

A discussion of the action of caustic and alk. earth alkalies, potash, soda, borax and Na phosphate. (C)

HOW TO REDUCE THE FAT REQUIREMENTS FOR THE FINISHING (OF TEXTILES). W. Pflumm. *Klepzig's Textil-Z.*, V. 43, P. 419–20 (1940); abs. in *C. A.*, V. 34, Col. 8292.

The use of fats can be decreased by substituting modern washing agents for soaps, applying mixts. of these modern washing agents with fat-free solvents and by utilizing the spinning fats already present in the textile. Calcns. show that 100 kg. of fat yield approx. 160 kg. of soap or 300 kg. of an alc. sulfonate, which are suitable for washing 5500 and 15,000 kg. of textile, resp. Thus the washing power can be tripled by converting the fat into a sulfonate rather than a soap. This difference in the washing power is still greater if hard water is used for washing. Lanaclarin is an example of a fat solvent that can be used with alc. sulfonates. Slight contaminations can be removed by adding mixts. of Gardinol and alc. sulfonates to the dyeing bath. (C)

INDIGOSOLS: ADSORPTION AND SUBSTANTIVITY. P. Ruggli and M. Stäubli. *Helv. Chim. Acta*, 1940, V. 23, P. 689–717; abs. in *J. T. I.*, Feb. 1941, V. 32, P. A58. (C)

IV. Research Methods and Apparatus

Alcohol Extracts from Fine Wool: Investigation of. H. C. Haller. *Am. Dye. Rptr.*, 1941, V. 30, No. 9, P. 221–22.

Results are summarized as follows: "With the evidence from this experiment we know that alcohol extracts from wool consist of proteins or in part or portion of the fiber itself. The tests for protein in the extracts and in the standard wool solution gave positive indication. The solubility of the extracts in water discards the oil theory and the acidic conditions disprove the soap angle. Evidently alcohol extractions on wool are a valueless guide to the completeness of a scouring job. The 'purifying' of wool fibers before being used for research work may alter the fiber sufficiently to give misleading final results." (C)

Color and Illumination in Photomicrography. O. W. Richards. *J. Biol. Phot. Assoc.*, Dec. 1940, V. 9, P. 77–86; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 58.

An elementary discussion is given of the nature of light and color and of the principles of illumination for photomicrography. (S)

Cross-Sectioning Microtome for Textile Fibers. Fred. A. Mennerich. *Rayon Text. Mo.*, Feb. 1941, V. 22, P. 68–9.

Describes the construction and method of operation of a new type of cross-sectioning microtome, which involves a unique principle of construction in the feeding mechanism, in that the micrometer screw, as it is turned, accentuates a lever, which reduces the imparted motion to the plunger in a two to one ratio. The instrument can be used for making thin cross-sections of hairs, wool, rayon and all other textile fibers. (C)

An Easily Constructed Photomicrographic Camera. W. R. Dracass. *The Microscope*, July–August, September–October 1940, V. 4, Nos. 7, 8, P. 193–196, 202–06; abs. in *Eastman Kodak Abs. Bull.*, March 1941, P. 97.

A method is described of constructing a vertical stand and camera for a microscope. The author drew the pattern for a vertical steel rod one inch in diameter which is screwed into a cast-iron base and had the base cast at a commercial foundry. Details are given for the construction of a wooden camera with bellows and light-lock. (S)

An Electrolytic Method for the Determination of the Basic Amino Acids in Proteins. A. A. Albanese. *J. Biol. Chem.*, July 1940, V. 134, P. 467–82; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 65.

A micromethod is presented for the determination of basic amino acids in hydrolyzates of 0.5 gm. to 1.0 gm. of protein. The procedure is based on the preliminary separation of these substances from the other products of protein hydrolysis by electrical transport. This is followed by separation of arginine as the flavianate. The flavianic acid in the filtrate from this precipitation is removed by electrolysis. Histidine is precipitated as the mercuric chloride complex. Lysine is estimated from the residual nitrogen. Evidence is presented for the purity of these fractions. Analyses of some proteins by this method are presented and the results compared with those obtained by other methods. (S)

V. Pure Science, Economics and Misc.

Acetylation of Cellulose: The Origin of Primary Acetone-Soluble Cellulose Acetate. T. Araki. *J. Soc. Chem. Ind. (Japan)*, August 1940, V. 43, P. 228–30; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 69.

(See *Monthly Abs. Bull.*, November 1940, V. 26, P. 588.) It was found that cellulose acetate containing 35% acetyl and 10% sulfuric acid can readily be converted into cellulose acetate containing 40 to 41% of acetyl and about 0.1 to 0.2% of sulfuric acid by treatment with acetic acid at 50° C. for from 2 to 4 hours. (S)

Amino-acid Solutions: Surface Tension. J. W. Belton and A. H. H. Twidle. *Trans. Faraday Soc.*, 1940, V. 36, P. 1198–1208; abs. in *J. T. I.*, March 1941, V. 32, P. A127. (C)

Aromatic Sulfonic Acids as Reagents for Amino Acids. D. G. Doherty, W. H. Stein, and M. Bergmann. *J. Biol. Chem.*, September 1940, V. 135, P. 487–96; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 65.

The solubility products of a large number of aromatic sulfonates of amino acids have been determined and tabulated. Suggestions are made concerning the use of some of these as analytical reagents for amino acids. (S)

Cellulose Derivatives: Use in Plastics. E. Ott. *Ind. Eng. Chem.*, 1940, V. 32, P. 1641–1647; abs. in *J. T. I.*, March 1941, V. 32, P. A127.

The author discusses the constitution and structure of cellulose, the influence of substitution on physical properties, the effects of plasticizers on cellulose derivatives and the effect of molecular size and shape on the physical properties of cellulose derivatives in relation to the use of cellulose derivatives as basic materials for plastics. (C)

The Cleaning of Air by Thermal Repulsion. J. C. Blacktin. *J. Soc. Chem. Ind.*, November 1939, V. 58, P. 334–38; July 1940, V. 59, P. 153–54; abs. in *Eastman Kodak Abs. Bull.*, March 1941, P. 117.

It has been found that hollow-latticed bodies act as thermal repulsors of considerable efficiency. The application of the principle to construction of experimental dust filters is recorded and constructional details and filtration efficiencies are given. (S)

The Constitution of Indigo on the Basis of Light-Absorption Measurements. G. Scheibe, H. Dörfling, and J. Assmann. *Ann. Chem.*, 1940, V. 544, No. 3, P. 240–53; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 64.

Comparisons of the absorption spectra of indigo, styrol-indigo, anethol-indigo, and n-n′-diethyl-indigo are graphically shown. The effects of various solvents are indicated. There are either no *cis-trans* configurations for styrol- or anethol-indigo, or, if they exist, they are not expressed in the light absorption as evidenced by *cis-* and *trans*-stilbene. Intermediate bands between red and blue exist for mixtures of solvents which give these distinct bands, indicating also no tautomeric change or difference in molecular magnitude. Distribution coefficients also indicate no molecular size differences between red and blue solutions. The change seems to be

associated with the environment which, in turn, affects the polarity of the molecule and the less polar the molecule the more it resembles in color that obtained for the dye in the gaseous form where the band is in the red. (S)

DETECTION OF ACID GROUPS IN NATIVE CELLULOSE BY SALT FORMATION WITH CRYSTAL VIOLET BASE. M. Rebek. *Kolloid Z.*, August 1940, V. 92, No. 2, P. 217–21; abs. in *Eastman Kodak Abs. Bull.*, Feb. 1941, P. 65.

Evidence is given to show that 0.04 per cent of native cellulose consists of free carboxyl groups which are capable of reacting with crystal violet, a basic dye. Schmidt (*Ber. deut. chem. Ges.*, 1935, V. 68, P. 542; 1936, V. 69, P. 366; 1937, V. 70, P. 2345) obtained 0.28 per cent acid groups, using conductometric methods. The author suggests that incomplete reaction occurs with crystal violet because of the variation in the "acid strengths" of the carboxyl groups in the material, and proposes that this strength distribution be measured on the basis of "crystal violet numbers." (S)

THE DISSOLUTION OF CHEMICALLY MODIFIED COTTON CELLULOSE IN ALKALINE SOLUTIONS. VII. The Solvent Action of Solutions of Trimethylbenzyl- and Dimethyldibenzyl-Ammonium Hydroxides (Tritons B and F). T. Brownsett and D. A. Clibbens.

Fractional solubilities of chemically modified cotton celluloses have been measured in solutions of trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides (Tritons B and F respectively). The solubility/concentration curves for these two bases at 20° C., like that for tetramethylammonium hydroxide, contain two maxima. The maximum solubility rises, and the concentration at which it occurs falls, when the temperature is lowered from 20° to 0° C. In this respect, the Tritons resemble all the other strong bases of which the cellulose solvent powers have been examined in this series of investigations. Triton F completely dissolves cotton cellulose in which the extent of chemical modification is no greater than that incidental to a careful chemical purification process ("unmodified cotton"). The first maximum in the solubility curve with Triton F occurs at a base concentration of about 1.9*N*, and this is lower than the normal concentration of maximum solvent power for any other base so far examined. A solution of unmodified cotton in Triton F can be diluted until the concentration of the base is as low as 0.5*N* without precipitation of the cellulose, though the solubility of cellulose in this concentration of Triton F determined by direct extraction is zero. At a given concentration of base, the solubility of modified cotton cellulose increases with the fluidity of its solution in cuprammonium, and the curve relating solubility at the optimum concentration to the fluidity of the cellulose affords the best measure at present available of the cellulose dissolving power of the base. By means of such curves, derived from measurements in this and previous papers, the solvent actions of six non-complex bases towards cellulose are compared at 20° C. or 15° C.

The viscosities of aqueous solutions of the same bases at 20° C. have been measured, and are recorded as functions of normal concentration. The order of cellulose dissolving power is approximately the same as that of the viscosities of the bases, the best solvents being those that yield the most viscous solutions at a given normal concentration. (C)